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(71)Applicant : TOKYO OHKA KOGYO CO LTD

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(72)Inventor : WAKIYA KAZUMASA
KOBAYASHI MASAICHI
TANAKA HATSUYUKI
NAKAYAMA TOSHIMASA

(54) COATING LIQUID COMPOSITION FOR CHEMICALLY AMPLIFIED RESIST

(57)Abstract:

PURPOSE: To prevent multiple interference in a resist film in lithographic processing by coating the chemically amplified resist film with the composition containing a water-soluble film-forming component and a proton generating substance to form a film on the surface.

CONSTITUTION: The water-soluble film-forming component can be embodied by a water-soluble polymer, such as hydroxypropylmethyl cellulose phthalate and a vinyl polymer like polyvinylpyrrolidone. Water-soluble polymers having no hydroxyl groups in the molecule, such as polyacrylate and polyvinylpyrrolidone, are preferable. As the proton generating substance, inorganic acid, such as hydrochloric acid and nitric acid, and organic acids, such as trifluoroacetic acid, are preferable. The water-soluble film-forming component and the proton generating substance are contained in an amount of 0.5-10weight%, and 0.01-1.0weight%, respectively.

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CLAIMS

[Claim(s)]

[Claim 1] The coating liquid constituent for chemistry magnification mold resists which contains a water-soluble film formation component and the proton generating matter, and changes.

[Claim 2] The coating liquid constituent for chemistry magnification mold resists according to claim 1 whose proton generating matter is an inorganic acid or an organic acid.

[Claim 3] The coating liquid constituent for chemistry magnification mold resists according to claim 1 or 2 which is that to which a water-soluble film formation component does not contain a hydroxyl group in a molecule.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This inventions are a new coating liquid constituent for chemistry magnification mold resists, and applying to the chemistry magnification mold resist film, and making a coat form in more detail, have the effectiveness of supplying a proton and relate to the coating liquid constituent for chemistry magnification mold resists which gives the pattern excellent in the cross-section configuration while they prevent the interference in lithography processing.

[0002]

[Description of the Prior Art] The method of forming the thin film of a photoresist constituent on a silicon wafer as micro processing by the photoetching method, and etching this silicon wafer in the manufacture process of semiconductor devices, such as IC and LSI, conventionally, through the mask pattern with which the pattern of a semiconductor device was drawn on it by using as a protective coat the resist pattern which developed negatives after irradiating activity beams of light, such as ultraviolet rays, and was obtained is taken.

[0003] By the way, while the degree of integration in manufacture of a semiconductor device increases quickly in recent years, in manufacture of a VLSI etc., the process tolerance of a submicron field or the field in quarter Miquelon which is overly a detailed pattern has come to be required. In connection with it, short wavelength-ization called excimer lasers, such as KrF laser, is further needed for i line from g line, and deep-UV, and the current chemistry magnification mold resist is most expected also for exposure wavelength as a resist for activity beams of light of short wavelength.

[0004] This chemistry magnification mold resist is a resist using the catalysis of the proton generated by exposure, has high sensitivity and high definition extremely, and has the advantage that a proton generating agent (sensitization agent) is little, and ends. There are two types of these chemistry magnification mold resists, a positive type and a negative mold, and the resist using the onium salt as a proton generating agent is known as a positive type, using what protected the hydroxyl group of a polyvinyl phenol by protective groups, such as a t-butoxycarbonyl group. On the other hand, the resist of three-component system which used the halogenide as a polyvinyl phenol and a proton generating agent, and used the melamine derivative for resin as a cross linking agent as a negative mold is put in practical use.

[0005] In such a chemistry magnification mold resist, when the resist film is exposed, the proton concentration of the front face is low, and the configuration of the resist pattern upper part obtained tends to become round, therefore the active species of etching are scattered about in the resist pattern upper part in the case of etching, and it has the fault that the exact imprint to the substrate substrate of a resist pattern is difficult.

[0006] Moreover, in the pattern formation using the photoresist film, there is a fault that generally light changes a pattern dimension with change of photoresist thickness in multiplex interference within the photoresist film as a result of [its] a lifting.

[0007] In the chemistry magnification mold resist, the approach of carrying out acid treatment of the

front face of for example, the chemistry magnification mold negative-resist film is tried as an approach of obtaining a rectangular resist pattern (open technical report number No. 2317 [92 to]). However, this approach processes the front face of the resist film for the solution of the acid concentration 0.001-0.5M with means, such as fuel spray, and it is the approach of forming the refractory-ized layer to an alkali development, and has a fault, like there is no effectiveness that uniform processing prevents multiplex interference of the light a difficult top and within the resist film.

[0008] On the other hand, the formation approach of the pattern which forms in a resist film front face, the transparency mold acid-resisting layer, for example, the polysiloxane layer, of the beam of light for exposure, is proposed (JP,60-38821,A). However, when an organic solvent must be used, this acid-resisting layer must be removed and many processes are required before carrying out a development although it is effective in preventing multiplex interference of the light within the resist film, even if it applies this approach to the chemistry magnification mold resist film, it cannot solve the fault resulting from the lowness of the proton concentration of that front face.

[0009]

[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation, is apply to the chemistry magnification mold resist film, is make a coat form in the front face, has the effectiveness supply a proton to homogeneity while prevent the multiplex interference in the resist film in lithography processing, and is make for the purpose of offer the coating liquid constituent for chemistry magnification mold resists which gives the pattern which was excellent in the cross section configuration.

[0010]

[Means for Solving the Problem] this invention persons came to complete this invention for the ability of that object to be attained based on a header and this knowledge with the constituent containing a water-soluble film formation component and the proton generating matter, as a result of repeating research wholeheartedly that the coating liquid constituent for chemistry magnification mold resists which has the aforementioned desirable property should be developed.

[0011] That is, this invention offers the coating liquid constituent for chemistry magnification mold resists which contains a water-soluble film formation component and the proton generating matter, and changes.

[0012] As a water-soluble film formation component used in this invention constituent A water-soluble polymer can be mentioned. This water-soluble polymer For example, hydroxypropylmethylcellulose phthalate, hydroxypropyl-methylcellulose acetate phthalate, Hydroxypropyl-methylcellulose acetate succinate, hydroxypropyl-methylcellulose hexahydro phthalate, The hydroxypropyl methylcellulose, hydroxypropylcellulose, Hydroxyethyl cellulose, cellulose acetate hexahydro phthalate, Cellulose type polymers, such as a carboxymethyl cellulose, ethyl cellulose, and methyl cellulose, N and N-dimethyl acrylamide, dimethylaminopropyl methacrylamide, N and N-dimethylaminopropyl acrylamide, N-methylacrylamide, Diacetone acrylamide, dimethylaminoethyl methacrylate, Although vinyl system polymers, such as acrylic polymers, such as diethylamino ethyl methacrylate, N, and N-dimethylamino ethyl acrylate, acryloyl morpholine, and an acrylic acid, polyvinyl alcohol, and a polyvinyl pyrrolidone, can be mentioned In these, the above-mentioned acrylic-acid system polymer, a polyvinyl pyrrolidone, etc. which do not have a hydroxyl group and which are a water-soluble polymer are suitable in a molecule, and especially a polyvinyl pyrrolidone can use it preferably. One sort of these water-soluble film formation components may be used, and they may be used combining two or more sorts.

[0013] On the other hand, as proton generating matter, an acid like an inorganic acid or an organic acid is desirable. As such an acid, organic acids, such as inorganic acids, such as a hydrochloric acid, a sulfuric acid, a nitric acid, and a phosphoric acid, a formic acid, an acetic acid, a propionic acid, benzenesulfonic acid, toluenesulfonic acid, and trifluoroacetic acid, can be mentioned, for example. In addition, weak acidic salts, such as an ammonium chloride, an ammonium nitrate, an ammonium sulfate, and ammonium phosphate, etc. can be used. One sort of these proton generating matter may be used, and it may be used combining two or more sorts.

[0014] this invention constituent is usually used in the form of a water solution, and, as for the content

of this water-soluble film formation component, it is desirable for there to be 0.5 - 10 % of the weight in 1 - 5% of the weight of the range preferably, and, as for the content of the proton generating matter, it is desirable that there is 0.01 - 1 % of the weight in 0.05 - 0.5% of the weight of the range preferably.

[0015] Although the coating liquid constituent of this invention is applied to the front face of the chemistry magnification mold resist film, there is especially no limit about the method of application and the approach of arbitration can be used, a spin coat method is usually advantageous.

[0016] The chemistry magnification mold resists to which the coating liquid constituent of this invention is applied may be any of a positive type and a negative mold.

[0017]

[Effect of the Invention] The coating liquid constituent of this invention can be applied to the front face of the chemistry magnification mold resist film, and can form the coat which contains the proton generating matter in homogeneity by drying. While the multiplex interference in the resist film is prevented in lithography processing by this, a proton is supplied and the pattern which is excellent in a cross-section configuration as a result is formed.

[0018]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0019] After dissolving mull Chinese quince car PHM-C(Maruzen Petrochemical Co., Ltd. make) 8.5g and 1.5g of methoxymethyl-ized urea-resins which are example 1 hydrogenation polyhydroxy styrene in 20g of ethyl lactates, the resist solution which dissolved and obtained 2-(p-methoxyphenyl)-4 and 6-screw (TORIKURORO methyl)-1,3,5-triazine 3g to this was obtained.

[0020] Next, the resist layer of 1.0 micrometers of thickness was formed by carrying out a spin coat for 20 seconds by 4000rpm, and drying for 90 seconds at 110 degrees C on a hot plate on the 5 inch silicon wafer which left this resist solution for 7 minutes, and carried out surface preparation into the hexamethyldisilazane ambient atmosphere. Subsequently, the spin coat of the solution which added the hydrochloric acid was carried out on the resist layer so that it might become concentration 0.25% of the weight to a polyvinyl-pyrrolidone water solution 2% of the weight, and the spreading layer of about 600A of thickness was obtained.

[0021] Next, by cutback projection aligner NSR-1755i7A for i lines (NIKON CORP. make), after exposing i line selectively, by performing heat-treatment for 90 seconds at 100 degrees C, and being immersed for 1 minute into a 2.38-% of the weight tetramethylammonium hydroxide water solution, dissolution clearance of the non-irradiating part of i line was carried out, and the resist pattern was formed. As a result of observing the cross-section configuration of the formed resist pattern with an electron microscope, the amount of [of a resist pattern] head did not become round, but the resist pattern of a rectangular cross-section configuration was obtained.

[0022] In example of comparison 1 example 1, except not forming a spreading layer on a resist layer, as a result of forming a resist pattern by the same actuation as an example 1 and observing the cross-section configuration, the amount of [of a resist pattern] head was the resist pattern of a round cross-section configuration.

[0023] After having dissolved mull Chinese quince car PHM-C(Maruzen Petrochemical Co., Ltd. make) 500g which is example 2 hydrogenation polyhydroxy styrene in dioxane 1500g, adding and stirring 11-tert-butyl dicarbonate 91.6g in this solution and dissolving thoroughly, it was dropped having triethylamine 63.6 bet it for about 30 minutes, and stirred as it is for 3 hours. After depositing resin by adding and stirring the pure water of the amount of 4 times to the solution furthermore obtained, it carried out the ** exception, and dehydrated and dried after washing with pure water.

[0024] Subsequently, 3g of one mol of 10g [of this resin], 2, 3 and 4, and 4'-tetra-hydroxy benzophenones and four mols [of 1 and 2-naphthoquinonediazide-4-sulfonyl chloride] esterification resultants was dissolved in 40g of ethyl lactates, and the resist solution was obtained.

[0025] Next, the resist layer of 1.0 micrometers of thickness was formed by carrying out a spin coat for 20 seconds by 3500rpm, and drying for 90 seconds at 110 degrees C on a hot plate on the 5 inch silicon wafer which left this resist solution for 7 minutes, and carried out surface preparation into the

hexamethyldisilazane ambient atmosphere. Subsequently, the spin coat of the solution which added the hydrochloric acid was carried out on the resist layer so that it might become concentration 0.3% of the weight to a polyvinyl-pyrrolidone water solution 4% of the weight, and the spreading layer whose thickness is about 700A was obtained.

[0026] next, the object for excimer lasers -- the exposure part of an excimer laser carried out dissolution clearance by performing heat-treatment for 90 seconds at 100 degrees C, and then being immersed for 1 minute into a 2.38-% of the weight tetramethylammonium hydroxide water solution by cutback projection aligner NSR-1505EX (NIKON CORP. make), after exposing an excimer laser selectively. As a result of observing the cross-section configuration of the formed resist pattern with an electron microscope, the rectangular resist pattern which was extremely excellent in the cross-section configuration was obtained.

[0027] In example of comparison 2 example 2, by the actuation as an example 2 that it is the same except not forming a spreading layer on a resist layer, as a result of forming a resist pattern and observing the cross-section configuration, the cross-section configuration of a resist pattern turned into a letter of overhanging, and the practical resist pattern was not obtained.

[0028] As a result of replacing with the water solution of the polyvinyl pyrrolidone and hydrochloric acid which were used in the example 3 example 1, forming a resist pattern by the same actuation as an example 1 except having used the solution which added the nitric acid so that it may become concentration 0.3% of the weight to a polyvinyl pyrrolidone water solution 2% of the weight, and observing the cross section configuration with an electron microscope, the amount of [of a resist pattern] head did not become round, but the resist pattern of a rectangular cross section configuration was obtained.

[0029] As a result of replacing with the water solution of the polyvinyl pyrrolidone and hydrochloric acid which were used in the example 4 example 1, forming a resist pattern by the same actuation as an example 1 except having used the solution which added trifluoroacetic acid so that it may become concentration 0.3% of the weight to a polyvinyl-pyrrolidone water solution 2% of the weight, and observing the cross-section configuration with an electron microscope, the amount of [of a resist pattern] head did not become round, but the resist pattern of a rectangular cross-section configuration was obtained.

[Translation done.]